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(54) **Olefin metathesis**

Verfahren zur Methathesis von Olefinen

Procédé pour la métathèse d'oléfines

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(56) References cited:  
**US-A- 3 696 163**

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## Description

The present invention relates to a process for the production of a mixture of butenes and propylene by metathesis of a feedstock comprising C5 olefins and ethylene.

It is well known that one of the by-products during the production of ethylene by steam cracking of liquid feedstock is a stream comprising C5 hydrocarbons which is known as "raw gasoline". This raw gasoline stream is conventionally subjected to hydrogenation to remove some of the dienes therein followed by distillation for separation into light and heavy gasoline streams. The lighter fraction is then further distilled to produce a C5 rich stream, the so-called "C5 light gasoline". Such a C5 light gasoline has a low octane number and is usually combined with a heavy gasoline stream to be added to conventional gasoline pools. Fluid catalytic cracking is another example of a process that produces a stream comprising C5 hydrocarbons.

It is also well known that due to environmental considerations, there is a serious demand for reduction in aromatic content and for minimising or eliminating lead additives of such gasoline. The reduction of these components in gasoline results in a significant loss of octane rating of the gasoline. Hitherto, this problem has been solved by incorporation of oxygenated compounds such as methyl tertiary butyl ether (MTBE) or ethyl tertiary butyl ether (ETBE) to the gasoline pool as high octane components. These components have excellent blending and vapour pressure characteristics and hence there is a great demand for such oxygenated compounds.

MTBE is produced by reacting isobutylene with methanol. Huge increases in the production of these raw materials have been observed and further accelerated growth is predicted. There are unlikely to be any problems with the production of methanol since the raw material which is natural gas is in plentiful supply and is relatively inexpensive. However, it is well recognised that the limiting step in the production of the aforementioned oxygenated compounds is the availability of isobutene.

Hitherto, isobutene has been produced by various routes including:

- a. Catalytic dehydrogenation of isobutane: the disadvantage of this process is the very high capital cost of the plant.
- b. Extraction of steam cracked C4 streams where the isobutene content thereof is first converted to MTBE and then back-cracked to substantially pure isobutene: this has the disadvantage that the main objective of the steam cracker is to produce ethylene and increasing the steam cracking temperature to maximise ethylene production will naturally reduce the isobutene content of the cracked gas.
- c. Fluid catalytic cracking (FCC): this has the disadvantage that the main function of an FCC unit is the production of transport fuels whilst minimising the formation of light ends; any light ends formed are converted to gasoline by alkylation.
- d. Isomerisation of butene-1: this has the disadvantage that butene-1 itself is produced either
  - i. by fractionation of a raffinate resulting from the conversion of isobutene in a mixed C4 stream to MTBE, or
  - ii. by extractive distillation of mixed butene streams, or
  - iii. by dimerisation of ethylene.

Of these, (i) is the most commercially viable and most economic. Butenes have also been produced by the disproportionation of olefins especially pentenes, particularly pentene-1 and pentene-2, and hexenes. In most cases these olefins are disproportionated on their own or in conjunction with other lower olefins such as propylene. Examples of prior publications describing such reactions include US-A-4331559, US-A-4291187, US-A-4269780, US-A-4071471, US-A-4262156, US-A-3761537, US-A-4922048, US-A-5191144, US-A-5264635 and J-A-48031194. None of these or other prior art references in this field disclose the metathesis of a feedstock comprising a mixture of C5 olefins and ethylene.

US-A-3696163 discloses a process in which isobutene is produced by contacting a cat gasoline feed with ethylene in the presence of a catalyst. However, the gasoline feed is not pretreated in any way.

It has now been found that the C5 light gasolines referred to above can be a valuable source of both isobutene and n-butenes which thereby not only enhances the value derivable from the light gasoline stream but is also a source of these C4 olefins and produces, in addition, propylene as by-product.

Accordingly, the present invention is a process for the production of a mixed C4 olefinic stream comprising primarily isobutene and butene-1, and propylene, said process comprising subjecting a mixed olefin feedstock comprising C5 olefins and ethylene to metathesis in the presence of a catalyst at a temperature in the range from -20°C to 200°C and subjecting the resulting metathesis product to fractionation to recover the mixed C4 stream and propylene resulting therefrom.

The feedstock for this reaction comprises C5 olefins and ethylene. The C5 olefins in the feedstock suitably comprise one or more of pentene-1, pentene-2, 2-methylbutene-2, 2-methylbutene-1 and 3-methylbutene-1. Such a feedstock may be obtained from a by-product during the steam cracking of naphtha to ethylene. This by-product usually

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comprises significant amounts of isomeric C5 paraffins, pentadienes, pentenes and small amounts of isomeric hexanes. When this by-product is subjected to a selective hydrogenation step followed by fractionation to remove C6 hydrocarbons, the resultant hydrogenated product comprises about 50% w/w of isomeric pentanes and about 47% w/w of isomeric pentenes but has virtually no pentene-1 or dienes. The selective hydrogenation step is suitably carried out in the presence of a conventional hydrogenation catalyst such as eg a nickel or palladium based catalyst. Two typical examples of such feedstock compositions from different refineries and the approximate concentration of the major components in such feedstocks are tabulated below:

TABLE 1

Component	Refinery A (Wt%)	Refinery B (Wt%)
n/i-Pentane	32	44
Cyclopentane	5	5.8
Pentene-1	2	8.2
Pentene-2	9	8.2
2-Methylbutene-1	3.6	5.6
2-Methylbutene-2	7.4	11.2
3-Methylbutene-1	0.5	1.3
Cyclopentadiene	9.1	7.4
Linear dienes	3	0.5
C6s	28.4	7.8

Taking a sample of an actual feedstock from Refinery A, the effect of deep hydrogenation followed by fractionation of the hydrogenated product to remove C6 hydrocarbons on the composition of the feedstock is shown in Table 2 below in which all units are % w/w of the total. As can be seen from Table 2, a feature of this hydrogenation step is that most, if not all, of the pentene-1 present in the original by-product is hydroisomerised to pentene-2 during this step. Furthermore, the original content of pentene-2 (8.43% w/w) and 2-methylbutene-2 (6.9% w/w) in the by-product is virtually doubled to 16.04% w/w and 17.1% w/w respectively in the hydrogenated product after the removal of the C6 components.

TABLE 2

Component	Untreated	Post Deep Hydrogenation	Post C6 Removal
n-Pentane	19.49	19.49	25.62
iso-Pentane	13.64	13.64	17.93
Cyclopentane	4.35	6.17	8.11
Pentene-1	1.99	0	0
2-methylbutene-1	3.68	0	0
3-methylbutene-1	0.53	0	0
cis-Pentene-2	2.1	3.99	5.25
trans-Pentene-2	6.33	8.22	10.81
2-methylbutene-2	6.9	11.11	17.1
Cyclopentene	9.09	10.91	14.34
1-cis-3-Pentadiene	0.56	0	0
1-trans-3-Pentadiene	0.84	0	0
1,4-Pentadiene	0.38	0	0
Isoprene	1.89	0	0
Cyclopentadiene	3.64	0	0
n-Hexane	5.74	5.74	0
2-Methylpentane	5.44	5.44	0
3-Methylpentane	2.32	2.32	0
2,3-Dimethylbutane	0.32	0.32	0
Cyclohexane	0	0	0
Methylcyclopentane	1.19	1.19	0
Benzene	1.06	1.06	0
Other C6's	7.65	7.65	0
Toluene	0.02	0.02	0

The ratio of the ethylene to C5 olefins in the mixed olefinic feedstock subjected to metathesis is suitably in the range from 1 : 1 to 10 : 1, preferably from about 1 : 3 to 1 : 6, eg 1 : 4 w/w. The use of excess ethylene suppresses the self metathesis of the C5 olefins.

The metathesis reaction is carried out in the presence of a catalyst. Examples of catalysts that may be used include a supported metal oxide such as an oxide of rhenium, tungsten, molybdenum or cobalt. The support may be alumina, silica, molybdena, zirconia or yttria. These supports may be dosed with other compounds capable of promoting the reaction such as eg phosphorus compounds, eg phosphates; tin compounds such as (alkyl)tin halides; and alkali and alkaline earth metals such as eg sodium, potassium and calcium. Supports such as alumina may be used in their various allotropic forms such as eg  $\gamma$ -alumina. The preferred catalyst is suitably rhenium heptoxide on alumina which may be phosphated alumina. The amount of metal oxide with respect to the support in the catalyst is suitably in the range from 0.1 to 15% w/w, preferably from 0.1 to 10% w/w, more preferably from 0.5% to 5% w/w. The process can advantageously use a metathesis catalyst comprising rhenium heptoxide on alumina (8% wt rhenium metal), prepared according to the teaching of US-A-4795734.

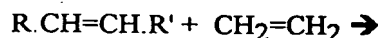
The metathesis reaction is suitably carried out under heterogeneous conditions. A solvent may be used as the reaction medium to keep the reactants and products in a liquid form, if this is desirable, although this may not be necessary where the reaction is carried out under pressure. A diluent which is inert under the reaction conditions may also be used, if desired. Examples of such diluents may be paraffinic or cycloparaffinic hydrocarbons.

The reaction is suitably operated under pressure so that the reactants and products are maintained in the liquid phase at the reaction temperature and under the reaction conditions. Thus, the pressures used may suitably range from 100 to 10000 kPa, preferably from 100 to 5000 kPa.

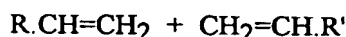
The metathesis reaction is suitably carried out at a temperature in the range from -20°C to 200°C, preferably from 0°C to 150°C and more preferably from 15°C to 40°C.

The reaction is not dependent upon the *cis*- or *trans*-configuration of the olefins and thus all pentene-2 present in the feed is available for the reaction.

The reaction is suitably carried out at a liquid hourly space velocity (LHSV) in the range from 1 to 30/hr by volume. The reaction may be typically represented by the following equation:



(I)



(II)

(III)

wherein R and R' represent various alkyl groups which, when taken together with the .CH=CH. functions in (I) above, represent isomeric C5 olefins. The products (II) and (III) shown above are two of the major products that are formed in the reaction. Typically, metathesis of pentene-2 and ethylene would give rise to a mixture of propylene and butene-1 whereas metathesis of 2-methylbutene-2 and ethylene would give rise to isobutene and propylene. Thus, the products of the metathesis reaction are a mixture of isobutene, butene-1 and propylene.

The products of the reaction can be fractionated to recover propylene on the one hand and a substantially pure mixture of isobutene and butene-1 on the other hand. The first distillate from the reaction mixture is of propylene and unreacted ethylene. The bottoms from this distillation step comprise a mixture of isobutene, butene-1 and unreacted C5 hydrocarbons. The bottoms may be fed to a second distillation stage where a mixture of isobutene and butene-1 are recovered overhead. The base products from this second distillation stage comprising unreacted C5 hydrocarbons is usually highly paraffinic and can therefore be used as a valuable steam cracker feed. The mixture of isobutene and butene-1 is difficult to separate by simple fractionation due to the close proximity of their boiling points (-6.9°C versus -6.3°C). This mixture may, however, be separated by reaction eg with an alcohol such as methanol or ethanol so that the isobutene is converted to the corresponding ether MTBE or ETBE leaving behind a substantially pure form of butene-1. The ether may be back-cracked to recover pure isobutene. Alternatively, butene-1 can be separated by absorption techniques. Pure butene-1 is a valuable feedstock for producing a number of compounds including *inter alia* polybutene-1.

The spent or deactivated catalyst from the reaction can be regenerated by thermal oxidation ie by heating at elevated temperatures above 300°C in the presence of oxygen or a gas containing oxygen.

A feature of this process is that the metathesis followed by fractional distillation produces a C4 stream containing only isobutene and butene-1. The production of MTBE or tertiary butyl alcohol or iso-butene sulphate from this C4 stream gives rise to substantially pure butene-1 as a by-product. This method therefore obviates the need separate butene-1 from butene-2 and conventional C4 saturated hydrocarbons as would be the case if a conventional MTBE raffinate had to be processed. Furthermore, the metathesis product of a feed comprising C5 olefins and ethylene is substantially free of undesirable butene-2, which is invariably present when ethylene in the feed is substituted by propylene.

The present invention is further illustrated with reference to the following Examples.

#### Example 1:

This Example illustrates the invention through conversion of a synthetic liquid feedstock containing 9.05% wt. of 2-methylbutene-2 in cyclohexane diluent with ethylene to produce iso-butene and propylene over a typical heterogeneous metathesis catalyst comprising rhenium heptoxide on alumina (8% wt rhenium metal), prepared according to the teaching of US-A-4795734.

The Example was carried out on a continuous basis using a fixed catalyst bed in a stainless steel reactor (32.5 mm internal diameter) located within an electric furnace. Reaction temperature was monitored using thermocouples located at the top and bottom of the catalyst bed. Metered gaseous and liquid reactants were fed upflow through the reactor. Gaseous and liquid products were separated on exit from the reactor and analysed using gas chromatography.

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Process conditions:

The metathesis catalyst (100 ml) was activated *in situ* in the reactor by heating for 12 hours at 550°C under an air purge (atmospheric press, GHSV = 500). After this oxidation stage, the reactor was purged at 550°C with nitrogen (atmospheric pressure, GHSV = 500) for 1 hour prior to cooling, under nitrogen, to the required start of run reaction temperature of 40°C.

The reactor was pressurised to the operating pressure of  $31 \times 10^5$  Pa (30 barg) with nitrogen prior to the introduction of the gaseous and liquid reactants. The nitrogen flow was replaced with ethylene, fed at the required rate for the reaction (44 litres/hr at NTP). The synthetic liquid feed was fed to the reactor at 150 ml/hr (LHSV = 1.5/hr. The approximate mole ratio of ethylene to C5 hydrocarbons is in the region of 10:1. A reactor pressure of  $31 \times 10^5$  Pa (30 barg) was maintained for the duration of the experiment. The average catalyst bed temperature was increased to approximately 51°C after 90 hrs on stream when 2-methylbutene-2 conversion had fallen to 50% of its start of the run value. The run was terminated after 128 hours on stream.

The results are shown in Table 3 below and are quoted on a mol% basis.

TABLE 3

2-Methylbutene-2 Metathesis with Ethylene								
TOS (hrs)	Av Bed Temp °C	2-MB-2 Conv.	iso-Butene Selec.		TOS (hrs)	Av Bed Temp °C	2-MB-2 Conv.	iso-Butene Selec.
18	41.2	81.3	71.83		70	40.1	47.45	94.27
19	41.1	79.26	74.31		73	40.2	47.70	91.31
20	40.9	83.77	73.62		76	40.1	46.59	87.32
21	41.1	77.62	74.31		79	39.9	47.14	93.33
22	41.1	74.09	74.16		82	39.9	47.31	93.99
24	41.1	71.93	77.98		88	39.9	37.77	99.37
26	41.1	69.91	82.81		91	48.3	37.82	85.71
28	41.1	78.22	82.62		93	50.9	59.45	84.89
30	41.2	73.44	93.35		95	51.5	60.71	86.88
32	41.1	72.18	82.83		97	51.3	52.76	91.54
39	40.4	65.15	86.11		99	51.3	48.86	85.17
41	40.8	71.77	87.75		101	51.3	47.22	89.41
43	40.8	67.28	82.2		103	51.6	46.62	93.19
45	40.7	56.82	89.56		105	51.3	36.37	98.21
47	40.6	64.83	88.81		109	51.4	40.63	92.64
49	40.6	62.23	91.81		111	51.5	37.97	96.04
52	40.5	60.01	85.87		116	51.5	29.15	92.32
55	40.5	59.79	92.31		119	51.8	31.16	89.82
58	40.4	54.98	94.64		122	51.9	26.19	100
61	40.4	52.14	96.33		125	52.1	26.11	100
67	40.3	49.81	82.99		128	52.9	28.06	98.98

These results show that isobutene was the only C4 olefin in the product. The reduction in selectivity was due to the formation of light polymer. These results demonstrate that the metathesis reaction between 2-methylbutene-2 and ethylene is very selective for the formation of isobutene as the only C4 olefin product.

**Example 2:**

This Example illustrates the invention through the production of butene-1, iso-butene and propylene by reaction of a synthetic liquid feedstock containing by weight 3.1% *trans*-pentene-2, 1.2% *cis*-pentene-2 and 7.8% 2-methylbutene-2 in cyclohexane diluent, with ethylene over an olefin disproportionation catalyst. The catalyst used was supplied by Engelhard de Meern BV (Ref Q195-01) and comprised typically 3% by weight of rhenium supported on 1.6 mm extrudates of alumina. The experiment was conducted on a continuous basis using a fixed catalyst bed in a stainless steel reactor (32.5 mm internal diameter) located within an electric furnace. Reaction temperature was monitored using thermocouples located at the top and bottom of the catalyst bed. Metered gas and liquid reactants were fed upflow through the reactor. Gas and liquid products were separated on exit from the reactor and analysed using gas chromatography.

The metathesis catalyst (100 ml) was activated *in situ* in the reactor by heating for 12 hours at 550°C under an air purge (atmospheric pressure, GHSV = 500). After this oxidation stage the reactor was purged at 550°C with nitrogen (atmospheric pressure, GHSV = 500) for 1 hour prior to cooling, under nitrogen, to the required start of run reaction temperature of 40°C.

The reactor was pressurised to the operating pressure of 3000 kPa (30 barg) with nitrogen prior to the introduction of the gas and liquid reactants. The nitrogen flow was replaced with ethylene, fed at the required rate for the reaction (24 l/hr. at NTP). The synthetic liquid feed was fed to the reactor at 75 ml/hr. (LHSV = 0.75/hr). A reactor pressure of 3000 kPa (30 barg) was maintained for the duration of the experiment. The reactor inlet (catalyst bed bottom) temperature was increased to approximately 51°C after 27 hours-on-stream (HOS) when 2-methylbutene-2 conversion had fallen to less than 50% of its start of run value. The run was terminated after 42 HOS. The results are shown in Table 4 below:

TABLE 4

HOS	2-MB-2 CONV.	c-Pentene-2 Conversion	t-Pentene-2 Conversion	i-Butene Selectivity	1-Butene Selectivity
2	64	92	81	66	68
8	55	97	88	64	65
14	50	94	73	57	65
42	10	31	12	96	55

The above results show that the primary product of the metathesis is a C4 olefinic stream comprising iso-butene and butene-1 with a mole of propylene being formed for each mole of the C4 olefin.

**Claims**

1. A process for the production of a mixed C4 olefinic stream comprising primarily isobutene and butene-1, and propylene, said process comprising subjecting a mixed olefin feedstock comprising C5 olefins and ethylene to metathesis in the presence of a catalyst at a temperature in the range from -20°C to 200°C and subjecting the resulting metathesis product to fractionation to recover the mixed C4 stream and propylene resulting therefrom, characterised in that the C5 olefinic feedstock is derived from a by-product during the steam cracking of naphtha to ethylene which comprises significant amounts of isomeric C5 paraffins, pentadienes, pentenes and small amounts of isomeric hexanes, and is subjected to a deep hydrogenation step in the presence of a hydrogenation catalyst followed by fractionation to remove C6 hydrocarbons.
2. A process according to Claim 1 wherein the C5 olefins in the feedstock comprise one or more of pentene-1, pentene-2, 2-methylbutene-2, 2-methylbutene-1 and 3-methylbutene-1.
3. A process according to any one of the preceding Claims wherein the ratio of the C5 olefins to ethylene in the mixed olefinic feedstock subjected to metathesis is in the range from 1 : 1 to 10 : 1
4. A process according to any one of the preceding Claims wherein the metathesis reaction is carried out in the presence of a catalyst comprising at least one supported metal oxide selected from the group consisting of an oxide of rhenium, tungsten, molybdenum and cobalt.

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5. A process according to Claim 4 wherein the support on which the metal oxide catalyst is supported comprises at least one of alumina, silica, molybdena, zirconia and yttria.
6. A process according to any one of the preceding Claims wherein the metathesis is carried out using a catalyst composition comprising rhenium heptoxide supported on alumina.
7. A process according to Claim 6 wherein the alumina support used is  $\gamma$ -alumina.
8. A process according to any one of the preceding Claims 5-7 wherein said support is dosed with a compound capable of promoting the reaction and selected from the group consisting of phosphorus compounds, tin compounds, alkali metals and alkaline earth metals.
9. A process according to any one of the preceding Claims wherein the amount of metal oxide with respect to the support in the metathesis catalyst is in the range from 0.1 to 10% w/w.
10. A process according to any one of the preceding Claims wherein the metathesis reaction is carried out under heterogeneous conditions.
11. A process according to any one of the preceding Claims wherein the metathesis reaction is operated under pressure so that the reactants and products are maintained in the liquid phase at the reaction temperature and under the reaction conditions.
12. A process according to any one of the preceding Claims wherein the metathesis reaction is carried out at pressures in the range from 100 to 10000 kPa and at temperatures in the range from -20°C to 200°C.
13. A process according to any one of the preceding Claims wherein the metathesis reaction is carried out at a liquid hourly space velocity (LHSV) in the range from 1 to 30 by volume per hour.
14. A process according to any one of the preceding Claims wherein the mixed butenes formed by the metathesis reaction are substantially free of butene-2.

### Patentansprüche

1. Verfahren zur Herstellung eines gemischten C4-Olefinstroms, umfassend vorwiegend Isobuten und Buten-1 sowie Propylen, wobei das Verfahren umfaßt Metathese einer gemischten Olefinbeschickung, die C5-Olefine und Ethylen umfaßt, in Gegenwart eines Katalysators bei einer Temperatur im Bereich -20°C bis 200°C und Fraktionieren des erhaltenen Metatheseprodukts unter Gewinnung eines gemischten C4-Stroms und dabei anfallenden Propylens, dadurch gekennzeichnet, daß die C5-Olefinbeschickung von einem Nebenprodukt während der Dampfrücklage von Erdöl zu Ethylen stammt, das bedeutende Mengen an isomeren C5-Paraffinen, Pentadienen, Pentenen und geringe Mengen an isomeren Hexanen umfaßt, und einem Tiefhydrierungsschritt in Gegenwart eines Hydrierungskatalysators, gefolgt von Fraktionierung zur Entfernung von C6-Kohlenwasserstoffen, unterzogen wird.
2. Verfahren nach Anspruch 1, wobei die C5-Olefine in der Beschickung eines oder mehrere von Penten-1, Penten-2, 2-Methylbuten-2, 2-Methylbuten-1 und 3-Methylbuten-1 umfassen.
3. Verfahren nach einem der vorangehenden Ansprüche, wobei in der gemischten, der Metathese zu unterziehenden Olefinbeschickung das Verhältnis der C5-Olefine zu Ethylen im Bereich 1:1 bis 10:1 liegt.
4. Verfahren nach einem der vorangehenden Ansprüche, wobei die Metathesereaktion in Gegenwart eines Katalysators, umfassend mindestens ein getragenes Metalloxid, ausgewählt aus der Gruppe, bestehend aus einem Oxid von Rhenium, Wolfram, Molybdän und Kobalt, ausgeführt wird.
5. Verfahren nach Anspruch 4, wobei der Träger, auf dem der Metalloxidkatalysator aufgetragen ist, mindestens einen von Aluminiumoxid, Siliziumdioxid, Molybdänoxid, Zirkoniumoxid und Yttriumoxid umfaßt.
6. Verfahren nach einem der vorangehenden Ansprüche, wobei die Metathese unter Verwendung einer Katalysatorzusammensetzung, umfassend Rheniumheptoxid, getragen auf Aluminiumoxid, ausgeführt wird.



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7. Verfahren nach Anspruch 6, wobei der verwendete Aluminiumoxidträger  $\gamma$ -Aluminiumoxid ist.
8. Verfahren nach einem der vorangehenden Ansprüche 5-7, wobei der Träger mit einer Verbindung, die die Reaktion fördern kann und die ausgewählt ist aus der Gruppe, bestehend aus Phosphorverbindungen, Zinnverbindungen, Alkalimetallen und Erdalkalimetallen, versetzt wird.
9. Verfahren nach einem der vorangehenden Ansprüche, wobei die Menge an Metalloxid hinsichtlich des Trägers in dem Metathesekatalysator im Bereich 0,1 bis 10% Gewicht/Gewicht liegt.
10. Verfahren nach einem der vorangehenden Ansprüche, wobei die Metathesereaktion unter heterogenen Bedingungen ausgeführt wird.
11. Verfahren nach einem der vorangehenden Ansprüche, wobei die Metathesereaktion unter Druck ausgeführt wird, so daß die Reaktanten und Produkte bei der Reaktionstemperatur und unter den Reaktionsbedingungen in der flüssigen Phase gehalten werden.
12. Verfahren nach einem der vorangehenden Ansprüche, wobei die Metathesereaktion bei Drücken im Bereich 100 bis 10 000 kPa und bei Temperaturen im Bereich -20°C bis 200°C ausgeführt wird.
13. Verfahren nach einem der vorangehenden Ansprüche, wobei die Metathesereaktion bei einer stündlichen Flüssigkeitsraumgeschwindigkeit (LHSV) im Bereich 1 bis 30 auf das Volumen pro Stunde ausgeführt wird.
14. Verfahren nach einem der vorangehenden Ansprüche, wobei die durch die Metathesereaktion gebildeten gemischten Butene im wesentlichen frei von Buten-2 sind.

### Revendications

1. Procédé pour la production d'un courant oléfinique en  $C_4$  mixte comprenant principalement de l'isobutène et du butène-1, ainsi que du propylène, ledit procédé consistant à soumettre une charge d'alimentation oléfinique mixte comprenant des oléfines en  $C_5$  et de l'éthylène à une métathèse en présence d'un catalyseur à une température comprise entre -20°C et 200°C et à soumettre le produit de métathèse obtenu à un fractionnement pour récupérer le courant d'hydrocarbures en  $C_4$  mixte et de propylène obtenu par fractionnement, procédé caractérisé en ce que la charge d'alimentation oléfinique en  $C_5$  est dérivée d'un sous-produit pendant le vapocraquage du naphte en éthylène qui comprend des quantités importantes de paraffines isomères en  $C_5$ , de pentadiènes, de pentènes et de petites quantités d'hexanes isomères, et qu'elle est soumise à une étape d'hydrogénation profonde en présence d'un catalyseur d'hydrogénation suivie par un fractionnement pour retirer les hydrocarbures en  $C_6$ .
2. Procédé selon la revendication 1, dans lequel les oléfines en  $C_5$  dans la charge d'alimentation comprennent un ou plusieurs éléments parmi le pentène-1, le pentène-2, le 2-méthylbutène-2, le 2-méthylbutène-1 et le 3-méthylbutène-1.
3. Procédé selon l'une des revendications précédentes, dans lequel le rapport des oléfines en  $C_5$  à l'éthylène dans la charge d'alimentation oléfinique mixte soumise à la métathèse est compris entre 1:1 et 10:1.
4. Procédé selon l'une des revendications précédentes, dans lequel la réaction de métathèse s'effectue en présence d'un catalyseur comprenant au moins un oxyde métallique sur support choisi dans le groupe formé par un oxyde de rhénium, de tungstène, de molybdène et de cobalt.
5. Procédé selon la revendication 4, dans lequel le support sur lequel le catalyseur d'oxyde métallique est supporté comprend au moins un élément parmi l'alumine, la silice, le molybdène, la zircone et l'yttria.
6. Procédé selon l'une des revendications précédentes, dans lequel la métathèse s'effectue en utilisant une composition catalytique comprenant l'heptoxyde de rhénium supporté sur l'alumine.
7. Procédé selon la revendication 6, dans lequel le support d'alumine utilisé est la  $\gamma$ -alumine.
8. Procédé selon l'une des revendications 5 à 7, dans lequel ledit support est dosé avec un composé capable de favoriser la réaction et choisi dans le groupe formé par les composés phosphorés, les composés de l'étain, les métaux

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alcalins et les métaux alcalinoterreux.

9. Procédé selon l'une des revendications précédentes, dans lequel la quantité d'oxyde métallique dans le catalyseur de métathèse par rapport au support est compris entre 0,1 et 10% p/p.

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10. Procédé selon l'une des revendications précédentes, dans lequel la réaction de métathèse s'effectue dans des conditions hétérogènes.

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11. Procédé selon l'une des revendications précédentes, dans lequel la réaction de métathèse est effectuée sous pression de sorte que les réactifs et les produits soient maintenus en phase liquide à la température réactionnelle et dans les conditions réactionnelles.

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12. Procédé selon l'une des revendications précédentes, dans lequel la réaction de métathèse s'effectue à des pressions comprises entre 100 et 10 000 kPa et à des températures comprises entre -20°C et 200°C.

13. Procédé selon l'une des revendications précédentes, dans lequel la réaction de métathèse s'effectue à une vitesse spatiale horaire de liquide (LHSV) comprise entre 1 et 30 en volume par heure.

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14. Procédé selon l'une des revendications précédentes, dans lequel les butènes mixtes formés par la réaction de métathèse sont essentiellement exempts de butène-2.

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